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PROCESS FOR MAKING COATING MATERIAL EMULSIONS

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In my British Patents 318,562, 321,692, and 341,490 as well as in my United States Patent 2,007,958, I have produced plastic masses out of fatty oils by the way of aggregating them in the form of aqueous emulsions. The basic idea of my development program at the time those patent applications were filed, was to convert fatty oils into a rubber-like stage, having properties similar to natural rubber. The products so obtained could be milled and compounded on rubber mills.

According to the present invention, I have prepared by new means aggregated fatty oil emulsions for use in protective coatings, such as varnishes, paints, enamels, etc. The emulsions dealt with in the present application I call "air sensitive emulsions." Under air sensitive emulsions I understand such emulsions, which are sensitive to the action of the air, when exposed to it in form of a thin layer, such as a film, e. g. of 0.0015" to 0.003" wet film thickness; insofar as they contain the fatty oils in the form of solid particles and on the action of the air on their thin layers, as soon as demulsification sets in, they form a solid and coherent film. Such solid film is formed also under such conditions under which a large percentage of the water, originally being the dispersion medium, is still occluded in the film. The film formation is usually reached within a couple of seconds, but latest in a couple of minutes and always in a shorter time than 30 minutes. The non-fluid stage is reached even earlier. In some exceptional cases it may be desirable to slow down artificially the film formation of air sensitive emulsions, so that the film formation should occur within a time exceeding 30 minutes, however, the film formation is rarely slowed to an extent that it should take more than 1 hour. If an air sensitive emulsion is rubbed between the fingers for a minute or so, it will also deposit solid particles or a solid film in between the fingers.

Briefly considered, the air sensitive emulsion of the present invention is prepared as an oil-in-water emulsion of which the dispersed phase incorporates a fatty acid ester, such as a fatty oil. The fatty oil is preliminarily bodied to a relatively heavy viscosity and then emulsified, and, in dispersed form, the particles of the fatty

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oil are treated to effect agglomeration, for instance, by employing hydrogen peroxide, or in other ways as more fully described here below. Advantageously the pH value of the emulsion is retained on the acid side and within certain limits during the aggregation treatment. The degree of prebodying and of aggregation of the dispersed particles in situ is such as to render the emulsion highly sensitive to the action of air when spread in thin films and thereby provide for the formation of a coherent solid film immediately upon demulsification of the emulsion.

To explain the importance of my new emulsions, I want to refer to the known facts that if drying oils are used to prepare coating materials, before they form a solid film, they undergo a comparatively slow drying process. Before they form a solid film, they remain for a long period in a liquid stage and reach the so-called "dust-free" stage after a considerable lapse of time. This property of drying oils is causing limitations in their use in protective and decorative coatings and in cases where rapid drying is needed it was necessary to use lacquers, such as nitro-cellulose lacquers. Such lacquers contain more expensive film-forming solids than drying oils and their solvents are also more expensive than those used in connection with drying oils. Now, my new emulsions enable the formulation of very fast drying, almost lacquer-like drying, coating materials, while using as principal film-forming solids drying and semi-drying oils, and utilizing water as principal dispersing agent.

It is old in the art to make emulsion paints, which contain drying oils and drying oil emulsions have been used for many diversified purposes in the past. However, my present invention does not deal with emulsions of drying oils in general, but with quite specific types of emulsions, containing drying oils or semi-drying oils. The dispersed phase of my emulsions has been aggregated and the emulsions possess qualities defined further above as inherent to air sensitive emulsions.

Many investigators consider the process I am calling as aggregation, as polymerization, but I am confident of the fact that actually what occurs in the emulsion is better defined with the expression used by me, that is, by "aggregation." (See article "Polymerization or Aggregation?"—National Paint Bulletin, October, 1937.)

STARTING MATERIALS

The process may be applied to fatty oils generally, including drying oils, semi-drying oils, and non-drying oils. A typical list of such oils follows:

Tung oil
Oiticica oil
Dehydrated castor oil
Linseed oil
Perilla oil
Sunflower oil
Poppyseed oil
Soya bean oil
Walnut oil
Rapeseed oil
Pineseed oil
Olive oil
Corn oil
Cottonseed oil
Coconut oil
Babassu oil
Hydroxylated oils such as castor oil, etc.
Fish oils (train oils)

It should be noted that, in addition to the natural glycerin esters of the fatty acids, other esters may be employed, such as synthetic glycerin esters of fatty acids, and fatty acid esters formed with other polyhydric alcohols, such as glycols, pentaerythritol, mannitol, sorbitol, etc. In short, natural or synthetic oils may be used, whether of animal or vegetable origin, as well as fractions of either type.

For convenience, all such materials and combinations are referred to herein merely as fatty oils.

As the reaction taking place in my process is a reaction of the polyhydric alcohol esters of unsaturated fatty acids, all such mixed ester type synthetic resins may be used as starting materials for my process, which comprise at least 50% unsaturated fatty acid esters, calculating such portion of the polyhydric alcohol radical into the ester, which is needed to form the esters with the unsaturated fatty acid content of the synthetic resin. Such synthetic resins are, for instance, the alkyd resins of the kind which are mixed esters of polycarboxylic acids and unsaturated fatty acids.

Examples of polycarboxylic acids, forming alkyd resins useful in my process are for instance:

Phthalic acid,
Maleic acid,
Succinic acid,
Malic acid,
Tartaric acid,
Fumaric acid,
Citric acid,
Adipic acid,
Sebacic acid,
Azelaic acid,
Suberic acid, etc., or
Anhydrides of such acids.

Examples of the unsaturated fatty acids, forming alkyd resins useful in my process are for instance:

Linseed oil fatty acids,
China-wood oil fatty acids,
Perilla oil fatty acids,
Oiticica oil fatty acids,
Dehydrated castor oil fatty acids,
Sunflower oil fatty acids,
Soyabean oil fatty acids,
Cottonseed oil fatty acids,
Corn oil fatty acids,
Fatty acids of fish oils (train oils).

The polyhydric alcohols, forming the esters useful as starting materials in this process, should be preferably at least tri-hydric, such as glycerine.

For the purposes of this specification under fatty acid esters I understand polyhydric alcohol esters of acids of fatty oils, which esters contain in their acid component at least 50% acids of fatty oils and which fatty oil acids comprise fatty acids having at least two double bonds. In this definition of fatty acid esters, there is included the group of drying and semi-drying fatty oils, further the group of synthetic oils and the group of alkyd resins, not containing more than 50% polybasic acids in their acid component.

Any appropriate mixtures or combinations of members of the above described classes may be treated, as desired.

The better drying a fatty oil is, the more suitable it is for my present process. I found that at least some of the fatty acids present in my oils should preferably contain more than one double bond in the molecule. This includes esters of the drying oil fatty acids and of the semi-drying oil fatty acids. I also found that esters of fatty acids having conjugated double bonds undergo easier my emulsion aggregation process, than fatty acids with isolated double bonds.

I found that the fatty oils here above described are suitable to my emulsion-aggregation only if they have at least a certain critical minimum viscosity or body. In other words, to be susceptible to the aggregation in aqueous emulsion, they have to be pre-bodied by the usual means, known in the art. Such bodying may be carried out for instance by heating the oil to heat-body temperatures, or by blowing the oil with a gas, such as air or oxygen at room or elevated temperatures. Other means of bodying are treatment with ultraviolet light, by exposure to an electric field, etc.

I found that my oils have to have a minimum viscosity of Q in the Gardner scale, but preferably they should have still higher viscosities, such as V or Z–1 on the Gardner scale, and I further found that if the viscosity is more than Z–6, my emulsion aggregation reaction is still easier to perform.

However, drying oils are used in coating materials not only as such, but also in a blended form together with natural and synthetic resins.

The natural and synthetic resins, useful in my present process, are known in the art as varnish resins and all of them are soluble directly, or after a suitable treatment in varnish oils.

As resin components of my air sensitive emulsions I may use many of the natural and synthetic resins, of which the following list are examples:

Rosin,
Esters of rosin with polyhydric alcohols, (glycerine, glycols, pentaerythritol, sorbitol, mannitol, etc.)
Congo,
Congo esters,
Other copals (e. g. kauri),
Cumar and indene resins,
Maleic anhydride-rosin-polyhydric alcohol, type maleic resins,
Rosin modified phenolic resins,
So-called pure phenolic resins,
Terpene resins, etc.

In case oil-resin blends are used as the dispersed phase of my emulsions, the oils and resins may be advantageously cooked together in the regular way as varnish solids are prepared in the varnish kettle. If in such a case unbodied oils are used

as starting material, it is difficult to establish what the viscosity of the oil is in the varnish cook, as the oil could not regularly be separated from the resin with which it forms a uniform blend. In such a case we measure the viscosity of the oil-resin mixture and because such mixture may frequently be too viscous to be measured directly in the Gardner scale, when we refer to the viscosity of the blend, we may have to express same related to a solution of the blend in question in an organic solvent, such as for instance, in mineral spirits, giving also the solid content of such a solution.

As a general observation, I may mention that fatty oils form more readily air sensitive emulsions in presence of resins, than in absence of resins. In other words, if we compare cooks at the same temperature and for gradually progressing times of cooking, we find that cooks in which resins are present, form earlier air sensitive emulsions, under otherwise comparative conditions, than fatty oils alone in absence of resins. This statement is meant to apply for such cases in which emulsions of various cooking times are compared and checked whether under comparative reaction conditions they could be aggregated to the state in which they yield air sensitive emulsions. The resin containing cooks can be converted into air sensitive emulsions with a shorter cooking time than the resin-free comparative oil cooks.

TREATMENT CONDITIONS

Bodying

The first step in my process is, as indicated above, the bodying of the oil. This is effected in any of several known ways, such as:

1. By heating the oil, at suitable bodying temperatures, above 200° C., and usually above 250° C., until the desired viscosity is attained. (Stand oils, polymerized oils, or heat bodied oils.)

2. By blowing air, oxygen or ozone over or through the oil to be thickened, either at room temperatures or at elevated temperatures. (Oxidized oils or air blown oils.)

3. By utilizing various gases, such as SO_2, H_2S, CO_2, N_2, etc. either to blanket the oils during heat treatment or to treat the oils directly by blowing or bubbling the gas through the oil, either with or without the use of heat. (Non-oxidized bodied oils.)

4. By treating the oil with ultra-violet rays. (Uviol oils.)

5. By treating the oil in an electrical circuit with a potential difference capable of yielding bodying (Voltol oils).

6. By bodying oils with modifying agents (polar compounds) as disclosed in my U. S. Patents Nos. 2,189,772; 2,213,944; 2,293,038; 2,298,270; 2,298,916; etc., and the various divisions and continuations thereof.

7. By heat-bodying under vacuum, occasionally coupled with a steam treatment to distill off free fatty acids.

Combinations of certain of these bodying techniques may be employed, as, for example, bodying with polar compounds in the presence of an electro-static field.

It is important to the attainment of best results that the oil should be bodied before emulsifying it and treating it in the emulsion in accordance with my invention. Even where the bodying is relatively slight some advantages may be realized, but the strikingly improved results of my preferred method are most readily produced if the oil is quite heavily bodied. The extent or degree of bodying may vary over a considerable range, depending upon the purposes in view. However, in one preferred practice of the invention, the range of bodying desirable before emulsion aggregation may be defined by limits, as follows:

In the first place, the oil should be bodied at least to a degree such that when heated to 160° C. with 4½% sulfur an irreversible gel will form within about 4 hours and most desirably within about 3 hours.

On the other hand, the oil preferably should not have a body heavier than that which would result in conversion to an irreversible gel in less than 15 minutes when vulcanized with ½% sulfur at 120° C.

It may be mentioned that these limits, as just defined, are applicable not only to emulsion-aggregation treatment of fatty oils themselves but also to similar treatment of fatty oils in admixture with resins, thereby yielding emulsion-aggregated varnish solids of the oleo-resinous type.

I prefer to define the desired viscosity as above described, because, in the light of present knowledge, it is easier to apply some such test than it is to separate the component parts of an oleo-resinous mixture in order to determine the viscosity of the oil alone.

In addition to the foregoing limits of the range of bodying, it may be mentioned that alternatively the preferable range of bodying of the oil may be expressed by any suitable viscosity scale. Thus, e. g., for natural oils a satisfactory range of bodying is from about 15 to 20 poises (Y on the Gardner scale) up to in the neighborhood of 800 poises (beyond the upper limit of the Gardner scale). For most purposes it will be found desirable to utilize a viscosity upwards of about 100 poises. The measurement of the desired body by viscosity scales will, of course, be best suited to the situation where the oil is bodied prior to admixture with a resin, as in the preparation of varnish bases.

The best viscosity for any particular oil or oleo-resinous mixture will be a function of several variables. To mention a few, the solid content and pH of the emulsion used, the temperature of treatment, the type of resin used, if any, the nature of the oil, the proportion of oil to resin, the effect desired, etc., will influence the degree of body to be employed. In each individual case, however, it is easy to determine the most favorable viscosity to use. After the proper viscosity has been determined, the desired conditions can readily be duplicated. For instance, one may simply note the appearance and the behavior of so much of the material as clings to the stirring paddle when it is lifted out of the kettle from time to time, such as flow and the lengths of the string formed, etc.

It should be remembered, of course, that different resins have diverse effects on the oil bodying. Allowances must be made for this fact in calculating the time necessary to attain proper bodying of a particular mixture, and it should also be realized that in a certain case it may be possible to proceed to the emulsion-aggregation treatment step before the viscosity of the mixture is as high as would be necessary in another case with a different oleo-resinous mix.

A further convenient method establishing the necessary critical minimum viscosity of my fatty acid esters is the ammonia test. The test comprises in immersing a small pill of the ester by

the aid of a glass rod into concentrated ammonium hydroxide solution kept in a test tube. Satisfactory viscosity is reached if the pill solidifies in the concentrated ammonia in not more than 5 minutes to such an extent that when pressed against the wall of the test tube by the glass rod, it should feel rubbery (elastic), dry and should not stick to the wall of the test tube.

The ammonia test is particularly suitable to determine the necessary critical viscosity limit in the case of oil-resin mixtures or in the case of alkyd resins, which very often do not have a ready flow at room temperature. Alkyd resins, as it is known, are very viscous and often form plastic solids at room temperature, if the polybasic acid content is considerable.

It should be mentioned that generally speaking esters containing fatty acids with conjugated double bonds have a lower critical minimum viscosity requirement from point of view of the emulsion aggregation process, than similar esters with isolated double bonds.

Aggregation Process

As described further above, it is a prerequisite to my process that the oils should have at least a certain critical minimum viscosity. If they reach that minimum viscosity, they may undergo the emulsion aggregation process.

My aggregating agent is oxygen. I believe that the active agent of my process is an electrically charged oxygen particle. However, I have no definite proof of that supposition. As not any and all oxygen may act in my process as aggregating agent, I shall refer to the oxygen which is suitable in my process as "active oxygen" and I believe that the particles of this active oxygen are most probably electrically charged.

In my co-pending applications, Serial No. 521,441, filed February 7, 1944, and Serial No. 522,803, filed February 17, 1944, I have described several means how to obtain my active oxygen. These co-pending applications deal with a somewhat related subject matter.

I can obtain my active oxygen in various ways. (1) I may use a peroxide, such as a metal peroxide or hydrogen peroxide, or an organic peroxide to supply my active oxygen to my emulsions. (2) I may blow oxygen or an oxygen containing gas, such as air, through my emulsions. (3) I may use the oxygen which is present in the water phase of my emulsion as adsorbed oxygen.

However, as the three kinds of oxygen above referred to do not act with equal velocity, auxiliary assistance may be needed in many of the cases.

I found for instance that the application of heat is accelerating the action of my aggregating agent (active oxygen). In fact, the application of heat is one of the roads which lead to activate the oxygen particles in my reaction. Temperatures above room temperature may be used for such activation and they should not exceed the boiling point of the emulsion to be treated. Usually temperatures between 50° C. and 80° C. are useful, but temperatures below 50° C. and above 80° C. may also be used, if other reaction conditions warrant such a procedure, but such temperatures should not exceed the boiling point of the aqueous dispersion.

Agitation of the emulsion also acts as an activating factor and it may advantageously be combined with the application of temperatures higher than room temperature. It is believed that the oxygen particles which are adsorbed in the aqueous phase of the emulsion may obtain electric charges by friction, caused by forced movement. Elevated temperatures themselves are increasing the movement of air particles adsorbed in water and agitation causes also an increase in the movement of adsorbed gas particles. The combination of agitation and heat causes increased and combined activation.

Another way to activate the adsorbed oxygen is by treating the emulsion with energy being in the form of radiating energy of various wave lengths, such as ultra-violet light, X-rays, etc., which are known to ionize air.

The application of vacuum, that is reducing the pressure over the emulsion, accelerates the emulsion aggregation process and helps to activate the oxygen particles present.

In case peroxides are used and oxygen is liberated in situ, further activation by agitation and/or heat is not a necessary requirement and the aggregation may be carried out in a satisfactory way, at room temperature and even at temperatures lower than room temperature. In case, however, only the oxygen present by natural adsorption in the aqueous phase is used for the aggregation process, it is necessary to activate same and temperatures higher than room temperature and preferably agitation are needed to complete the reaction within practically useful time intervals.

If blowing of air or oxygen through the emulsion is used as a source of the aggregating active oxygen, the conditions are usually in-between the above-mentioned two extremes, on one end of using peroxides and on the other end of using the oxygen adsorbed in the water as sole aggregating agent. Whether heat and agitation should be used in connection with blowing air or oxygen through the emulsion, may depend on the particular reaction conditions involved, on the fineness of sub-dividing the gas bubbles used, the body and nature of the oil or oil-resin mixture, amongst others. It may be mentioned as a general rule, however, that under otherwise equal conditions peroxides act fastest, blowing of air or oxygen is next fast, and using the adsorbed oxygen only, is the slowest of the three alternatives. Further, it may be stated that under any condition agitation and/or heat accelerate the action of the oxygen and that their use is essential only in the slowest range.

With regard to the quality of the film-forming solids, the films which have been produced by the smallest possible quantity of active oxygen are most desirable, as they contain very little chemical oxidation products, whereas in cases where peroxides are used in considerable proportions, the active oxygen may cause chemical oxidation, yielding by-products, which are in many cases undesirable components of films obtained from coating compositions.

Critical Hydrogen Ion Concentration

One of the important criterions of my process is the pH of the emulsion. I found that it is important to have critical pH limit to carry out my process satisfactorily.

In my co-pending applications, Serial No. 521,441 and Serial No. 522,803, I described various pH ranges to achieve emulsion aggregation of my esters. In the present process I found that special advantages derive from the fact that the emulsion aggregation process is carried out on the acid side.

The reaction is greatly accelerated by a pH not exceeding 5.7. However, for many purposes I found that it is advantageous to have a pH which does not exceed 4, such as for instance a pH of 2.8.

Several advantages may be obtained, if the emulsion aggregation process is carried out according to this invention on the acid side, that is in a pH range below 7.

One advantage is, for instance, that when working on the acid side, the pH of the emulsion remains constant and does not drop. This is in contrast to observations made, when the emulsion aggregation is carried out on the alkaline side. In the latter case the pH drops regularly and it is difficult to keep the emulsion stable by either adding ingredients increasing the pH, and/or by using emulsifying agents which are active both on the alkaline and on the acid side. Without such precautions the emulsion may easily break. However, if the emulsion aggregation process is carried out according to the present invention on the acid side, the pH remains stable and it is easy to stabilize the emulsion. Further, the selection of emulsifying agents is also simplified.

A further advantage of the present process is, that the emulsion aggregation may be carried out in absence of driers. It has been found that when working on the acid side the addition of driers is unnecessary. In fact driers may retard the emulsion aggregation process, when working on the acid side. For many purposes it is advantageous to have films of coating materials containing fatty oils, which do not contain metallic driers. Such films, not containing metallic driers have better aging qualities and may be used with advantage as ingredients of lacquer emulsions, or may be mixed with lacquer emulsions, to form new types of coatings. Presence of metallic driers causes all kinds of complications in connection with simultaneous use of lacquers and fatty oils. Difficulties here referred to are well known to those skilled in the art.

Concentration of the Emulsion

I also found that the concentration of my emulsions, to be aggregated, is important and as a general rule lower solid content will accelerate the reaction, whereas higher solid content will retard same. A particularly advantageous range is between 10% and 20% solids. Vehicles of coating materials should preferably have solids in the neighborhood of 50% or more. It is possible to carry out the emulsion aggregation process in the neighborhood of 50%, or in other words, air sensitive emulsions can be produced in emulsions having 50% solids. In fact, even higher solids going up to 70% may be applied. However, the more concentrated emulsions we use, the more accelerating and activating conditions we have to apply for satisfactory results. For instance at a 20% concentration it is easy to apply the reaction using the adsorbed oxygen only, as aggregating agent, with comparatively low temperatures and slow agitation. However, using higher concentrations it may become necessary to use peroxides as activating agents and if the concentration is still further increased, the simultaneous use of peroxides and heat and agitation may be required to secure the transformation desired.

It may be advantageous to carry out my process in an emulsion with low solid content, to accelerate the process and after the emulsion aggregation is completed, to concentrate the comparatively dilute emulsion. Such concentration may be carried out by any of the means known in the art in connection with concentrating emulsions, for instance, concentrating natural rubber latex. One example of such a method is electrodecantation.

Oxygen Supplying Agents

As mentioned further above, if other reaction conditions are proper, the oxygen content of the water, present in the emulsion, may be satisfactory.

Oxygen may be supplied to the emulsion in form of oxygen gas or oxygen containing gases, such as air, by bubbling through the emulsion such gases or by introducing them by known means. Ozone may also be used.

To produce oxygen in situ peroxides or other per-compounds may be used. In most of the examples hydrogen peroxide is used to illustrate the addition of per-compounds. However, other peroxides may also be used, such as sodium peroxide, barium peroxide, magnesium peroxide, zinc peroxide, other metal peroxides, or organic peroxides, such as benzoyl peroxide, urea peroxide, etc. Examples of per-compounds are further perborates, percarbonates, persulfates, such as potassium, sodium and ammonium persulfates, perchlorates, pyrophosphate peroxides, ozonides, etc. The criterion of the usefulness of these agents is that they should supply oxygen in situ under the reaction conditions applied in my process and that the emulsion could be prepared in such a way that it should not break in their presence.

Emulsifying Agents

Great variety of emulsifying agents may be used in my process. A list of such emulsifying agents is given, for instance, under the title of Surface-Active Agents in the January, 1943, issue of Industrial and Engineering Chemistry, on pages 126 to 130.

A list of some emulsifying agents is given herewith:

Trade Name and Source	Manufacturer's Description
Duponol ME, E. I. du Pont de Nemours & Co.	Fatty alcohol sulphate.
Aerosol OT, American Cyanamid Company.	Dioctyl ester of sodium sulphosuccinic acid.
Emulphor AG, General Dyestuff Corporation.	Polyethyleneoxide condensation product.
Nekal A, General Dyestuff Corporation.	Sodium salt of alkyl-substituted naphthalene sulphonate.
Igepon, General Dyestuff Corporation.	Sodium sulphonate of an oleic acid ester of an aliphatic compound, for instance, of the type of $C_{17}H_{33}CON—CH_2C_2H_4SO_3Na$.
Triton, Rohm & Haas	Sodium salt of aryl alkyl poly ether sulphonate.
Emulgor A, Glyco Products	A highly polymerized glycol ester.
Wetanol, Glyco Products	Modified sodium salts of sulphated fatty alcohols.
Darvan #1, R. T. Vanderbilt Company.	Polymerized sodium salts of alkyl naphthalene sulphonic acids.
Hornkem, Hornkem Corp.	Purified sulpholignin—.
Beta Sol, Onyx Oil & Chemical Company.	Quaternary ammonium salt.
Pentamul 126, Heyden Chemical Corp.	Pentaerythritol monooleate.
Pentamul 147, Heyden Chemical Corp.	Pentaerythritol monolaurate.

I found that from the various emulsifying agents, for my present process, such types are most suitable, which are active on the acid side. The non-ionic emulsifying agents belong to that class, such as for instance, Pentamul 126 and 147, nonaethyleneglycolmonooleate, or the corresponding dioleate, or the corresponding monolaurate or dilaurate or monoricinoleate or diric-

inoleate. (Glyco products.) A further satisfactory group is the one of the cation-active emulsifying agents. Examples are the quaternary ammonium salts. As will be seen, the fatty alcohol sulphates (for instance, Duponol ME) are also suitable for my process.

EXAMPLES

The examples given here below illustrate my process and my products. I do not intend, however, to limit my products and my process to the scope of the examples given.

In many of the examples it was decided to determine the state of the dispersed phase of the emulsions and the progress of the emulsion aggregation reaction by coagulating the emulsions or sample portions thereof. This was done by the addition of a saturated barium chloride solution, which coagulates the emulsions, for instance emulsions made with Duponol ME, with ease. The resulting coagulum contained the dispersed phase of the emulsion, together with a small percentage of the water.

The appearance and condition of the coagula permits to classify same into one of the following classes:

1. FV, fluid and viscous.
2. HV–TP, heavy, viscous but still thermoplastic.
3. IG–CF, intermediate stage, having slight gel structure, but still showing cold flow characteristics.
4. NT–ST, a non-thermoplastic gel, soft and having considerable tack (NT–ST, for non-thermoplastic, soft and tacky).
5. GD, a gel stage, dry and free of tack.

The coagula were dried at elevated temperatures, to drive out any residue of water and the resulting solids were classified into one of the above designated classes.

In many of the examples here below, this classification was used to express the state of the dispersed phase of the emulsions.

In the examples following here below in all instances the nature of the process and its variables are demonstrated, instead of showing how to make a coating composition.

It should be mentioned that in all these examples where at least stage 4 (a non-thermoplastic gel) has been reached, the emulsion is an air sensitive emulsion, which can be used itself as a coating composition or which may be used as a component of coating compositions. (Obviously, where stage 5 has been reached, the reaction is more advanced and the emulsions are suitable in coating compositions.)

Comparative Examples 1 to 5.—Variation of pH Without Peroxide Addition

Example 1—Master batch

In these comparative experiments a very heavily bodied linseed oil was used, which is known in the art as OKO M–37 oil. This product is obtained by bodying linseed oil under vacuum, has a viscosity of approximately 800 poises and has a low acid value. As emulsifying agent 1% of Duponol ME dry was used, based on the weight of the oil to be emulsified. Distilled water was used as dispersion medium and the emulsion had a solid content of 20% by weight. The emulsion was made by adding a 10% solution of the Duponol ME to the oil and adding the water in small portions under agitation, until a uniform emulsion resulted before the addition of the next increment of the water. The emulsions so obtained showed satisfactory stability both in the acid and in the alkaline regions of varied pH values.

The emulsions were stirred by slow speed agitators at a temperature of 60° to 65° C. 500 grams of the emulsion were used in two-liter beakers. The beakers were covered, as much as possible, even if not air-tight, to prevent excessive evaporation and what evaporation still did occur, was compensated for by small additions of water from time to time.

It has been found that the hydrogen ion concentration has a paramountly important role in the conversion process yielding air sensitive emulsions. Studies were made in a wide range of hydrogen ion concentration. The following three examples were in the acid region and contained phthalete buffers.

The following preparations were made to produce emulsions with various pH values on the acid side:

3,000 grams of the master batch emulsion of Example 1 were prepared in such a way that it should contain the reaction product of 14.8 grams of phthalic anhydride and 2.0 grams NaOH, 1.2 times, dissolved in water. The emulsion so prepared had a pH of 2.8. The following preparations were made with this batch:

Example 2

500 grams of the emulsion of Example 1, containing phthalate buffer as described here above, unchanged, pH 2.8.

Example 3

500 grams of emulsion of Example 1, containing phthalate buffer as described here above, plus 0.8 gram NaOH, pH 4.8.

Example 4

500 grams of emulsion of Example 1, containing phthalate buffer as described here above, plus 1.0 gram NaOH, pH 5.7.

Example 5

A similar emulsion to the one of Example 1 was prepared directly to yield a pH of 7.1. 200 grams of M–37 oil, 20 grams of a 10% Duponol ME solution, 5.5 grams of $Na_2HPO_4.12H_2O$, 780 grams of water, and 1.2 grams NaOH were used in preparing the emulsion, pH 7.1.

All the emulsions were heated to 60°–65° C. and kept at that temperature continuously for 96 hours, under constant agitation of approximately 45 R. P. M. Samples were taken out from the emulsions at various intervals and the same were coagulated to check the progress of the reaction.

To give a few details, it should be mentioned that the emulsion with pH 2.8 reached after 16 hours a stage which was almost 4 on my scale (NT–ST), and was in between stages 4 and 5 after 96 hours. Whereas the emulsion with pH 7.1 was after 40 hours in stage 1 and reached after 96 hours a point below stage 3.

The examples have shown that conversion at a pH of 7 was practically nil and at a pH of 5.7 was slow. It seems that there is a very ineffective region between a pH of 5.7 and 8.4 or in their neighborhood.

The pH of the emulsions on the acid side remained fairly constant.

It should be emphasized that to none of the emulsions dealt with in this series was any peroxide or per-compound added.

EXAMPLE 6.—PEROXIDE VS. NO PEROXIDE AT VARYING pH VALUES

Six portions of the master batch emulsion of Example 1 were used in the present example. The pH of all six portions was adjusted by the addition of NaOH, to be 12.2. The following were the individual characteristics of the six portions:

6-A.—This batch was acidified and buffered with sodium acid phthalate. The pH was adjusted to 2.8.

6-B.—Acidified and buffered with sodium acid phthalate, adding 2½% of hydrogen peroxide based on the oil content of emulsion. The pH of this example was also adjusted to 2.8.

6-C.—Acidified with sodium acid phthalate and pH adjusted to 5.7.

6-D.—Acidified with sodium acid phthalate and treated with 2½% hydrogen peroxide, based on the oil content. The pH of this example was also adjusted to 5.7.

6-E.—This batch was rendered approximately neutral with mono-sodium phosphate.

6-F.—This batch was rendered approximately neutral with mono-sodium phosphate and treated with 2½% of hydrogen peroxide, based on the oil content.

In the above 6 experiments, there are actually 3 parallel experiments, investigating at various pH ranges differences if hydrogen peroxide is used or eliminated. The total treatment time in each case was 96 hours and sample quantities of each emulsion were coagulated after 16 hours, 40 hours, and 96 hours in each of the 6 individual cases. These 6 preparations were kept at 60° C. to 65° C. temperatures, replacing the water from time to time, which evaporated. The following table summarizes the readings.

TABLE A

Example	Per cent H_2O_2	pH	After 16 hr. treatment	After 40 hr. treatment	After 96 hr. treatment
6-A	None	2.8	(IG-CF) to (NT-ST).	(NT-ST)	(NT-ST) to (GD).
6-B	2.5	2.8	(NT-ST)	(NT-ST)+	(GD).
6-C	None	5.7	(FV)	(HV-TP)	Almost (NT-ST).
6-D	2.5	5.7	(FV)	(HV-TP)	(NT-ST).
6-E	None	7.2	(FV)	(FV)	(IG-CF) to (NT-ST).
6-F	2.5	7.1	(FV)	(IG-CF)	(NT-ST).

The 6 examples of this comparative series show the following conclusions: In the acid region the transformation is very slow near the neutrality point, fairly slow around the pH of 5.7, and somewhat faster at the pH of 2.8. Near the neutrality point around the pH of 7.2 the addition of hydrogen peroxide does not accelerate the conversion to a great extent. The presence of hydrogen peroxide does not show appreciable results at a pH of 5.7 either. However, at the pH range of 2.8, the addition of hydrogen peroxide is definitely accelerating the conversion.

The results permit the generalization that the hydrogen ion concentration is of primary importance and only where the hydrogen ion concentration is favorable can the right effect of hydrogen peroxide be noted. These conclusions obviously have to be limited to the actual reaction conditions used in these examples.

EXAMPLES 7 TO 10.—THE USE OF METALLIC DRIERS

In the standard way of emulsification, described in Example 1, four different preparations were made, having the following formulae:

Example 7

	Grams
M-37 linseed oil	100
10% Duponol ME solution	10
Distilled water	400
KH_2PO_4	1

Example 8

	Grams
M-37 oil	100
Naphthenate drier 6% cobalt metal content	0.5
10% Duponol ME solution	10
Distilled water	400
KH_2PO_4	1

REMARK: Examples 7 and 8 were parallel experiments, Example 8 having a metallic drier dispersed in the oil prior to emulsification.

Example 9

	Grams
M-37 linseed oil	100
10% Duponol ME solution	10
Distilled water	400
Hydrochloric acid, concentrated	1

Example 10

	Grams
M-37 linseed oil	100
Naphthenate drier 6% cobalt metal content	0.5
10% Duponol ME solution	10
Distilled water	400
Concentrated hydrochloric acid	1

REMARK: Examples 9 and 10 were parallel experiments, Example 10 having a metallic drier dispersed in the oil prior to emulsification.

All emulsions from 7 to 10 were agitated, while kept at temperatures ranging from 60° to 65° C., the treatment being carried out for 48 hours. Sample portions of the emulsions were coagulated after 24 hours and 48 hours treatment time, using barium chloride for precipitation, and the oil products were dried at 130° C. Table B shows the results of this series.

TABLE B

Example Number	Original pH	Coagula After 24 hours, Stage	Coagula After 48 hours, Stage
7	6.2	1-2 (FV) to (HV-TP)	Almost 4, Almost (NT-ST).
8	6.0	1 (FV)	3-4 (IG-CF) to (NT-ST).
9	1.8	3 (IG-CF)	4 (NT-ST).
10	1.6	1-2 (FV) to (HV-TP)	3+(IG-CF)+.

In the above table, where two stages are given combined with "to," this means that the product was in between the two stages in question. The same applies when two numbers are combined by a hyphen. Similar system was used in Table A.

Table B shows, that in the slightly acid and in the strongly acid regions, the addition of drier retarded the conversion. This retardation in the strongly acid region was more pronounced, which may be partly due to the fact that the conversion is much more rapid in the strongly acid region, or in other words, is very slow in the slightly acid region.

Examples 7 and 9 yielded after 48 hours treatment air sensitive emulsions.

GENERAL REMARKS

(*a*) In my Patent 2,007,958, I prepared rubber-like masses, out of bodied oils, which contained a metallic soap before emulsification. Such metallic soaps either were incorporated into the oils to form solidified oils, by direct addition, or the metallic soaps were formed in situ from salts, during heat bodying of the oil. Examples of the latter alternative are carbonates, sulphides and sulphites, which form soaps with the fatty oils at heat bodying temperatures, while evolving CO_2, or H_2S, or SO_2 gas.

I found that where a soap (e. g. a metallic soap) is incorporated in a heat bodied oil and such an oil is used in preparing coating materials, the films obtained have reduced water resistance, apparently because the soaps remaining in the films cause a constant swelling or even re-emulsification of the film. Therefore, in my present process I use with preference soap-free fatty oils and obtained thereby satisfactory weathering qualities of the films deposited from my coating composition.

(*b*) The Gardner scale, used in this specification is described in detail on page 217 of the 9th edition (1939) of "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," by Henry A. Gardner, published by the Institute of Paint and Varnish Research, 1500 Rhode Island Avenue, N. W., Washington, D. C.

(*c*) It should be mentioned, summarizing some aspects of this invention, that in case no oxygen addition is used to bring about the emulsion aggregation, in addition to the oxygen adsorbed in the water, the products so obtained are much more durable, as they are free of splitting-off products, caused by oxidation and also free of oxidation products of the ester molecule. Oxidation products in general are undesirable in coating materials, as they reduce water resistance and the life of the film.

It is of advantage if the oxygen content of the esters of my invention does not increase during the emulsion aggregation process to an extent larger than ½%, when compared to the oxygen content of the ester prior to emulsification.

(*d*) Flat wall paints made according to my process should preferably have a pigment volume ratio of 35% or more.

(*e*) The esters used in my emulsion aggregation process are always thermoplastic before emulsification, which means that they are either in a fluid state at room temperature or can be reversibly fused to form a liquid.

(*f*) The organic solvents I may use in my process are of the type, which are immiscible with water and which dissolve the esters and/or resins present in the dispersed phase of my emulsions.

(*g*) The air sensitive emulsions of the present process may be mixed with other emulsions, to form coating materials. Also pigments may be added to them by grinding or by other known means, to form emulsion paints or emulsion enamels. It is also possible to disperse the pigments in the oil containing emulsion solids, prior to emulsification.

(*h*) With regard to the question of activating the adsorbed oxygen, I wish to recapitulate that application of heat, agitation, the application of vacuum, and the treatment with oscillating energy, further the use of low solid content emulsions, are the factors, which seem to achieve this desired effect.

(*i*) With regard to the ammonia test, I wish to mention that whereas in the case of a positive ammonia test the starting materials for this process are always suitable for the emulsion aggregation, in most cases the degree of bodying necessary for the emulsion aggregation process is reached earlier than the ammonia test becomes positive.

I claim:

1. The process in preparing oil-in-water type air sensitive emulsions of fatty oils, which yield solid and coherent films upon demulsification, consisting of the steps of (1) bodying the fatty oil to a viscosity of at least Q on the Gardner scale, said bodied fatty oil showing flow characteristics at room temperature, (2) emulsifying said bodied fatty oil in water by the aid of an emulsifying agent which is stable on the acid side of the pH range, (3) bringing the pH to a range not exceeding 5.7, and (4) increasing the viscosity of the dispersed phase of the emulsion by the aid of active oxygen.

2. The process of claim 1, in which the pH of the emulsion in step (3) does not exceed 2.8.

3. The process of claim 1, in which the fatty oil is bodied to at least Y on the Gardner scale, prior to emulsification, and an oxygen evolving compound is used as a source of the active oxygen.

4. The process in preparing oil-in-water type air sensitive emulsions of soap-free bodied esters of a polyhydric alcohol formed with acids of fatty oils, said esters having in a fatty acid part of the molecule more than one double bond, said emulsion being useful in coating materials, consisting of the steps of (*a*) bodying the ester at least to a degree such that when heated to 160° C. with 4½% sulfur an irreversible gel will form within about 4 hours, but not beyond a degree to have a body heavier than that which would result in conversion to an irreversible gel in less than 15 minutes when vulcanized with ½% sulfur at 120° C., (*b*) emulsifying said bodied ester in water by the aid of an emulsifying agent which is stable on the acid side of the pH range, (*c*) bringing the pH of the emulsion to a range not exceeding 4, and (*d*) increasing the viscosity of the dispersed phase of the emulsion by the aid of an oxygen evolving compound.

5. The process of claim 4, in which the oxygen evolving compound is a peroxide.

6. The process of claim 4, in which the oxygen evolving compound is hydrogen peroxide.

7. The process of claim 4, in which the dispersed phase of the emulsion comprises a varnish resin, in addition to an ester of the fatty oil type.

8. The process of claim 4, in which the bodied ester content of the emulsion does not exceed 20% while step (*d*) is carried out.

9. The process of claim 4, in which step (*d*) of the process is carried out at temperatures rang-

ing from 50° C. and the boiling point of the emulsion.

10. The process of claim 4, in which step (*d*) of the process is carried out while the emulsion is mechanically agitated.

11. The process of claim 4, in which step (*d*) of the process is carried out under reduced pressure.

12. The process of claim 4, in which the bodied ester is a heat bodied fatty oil, having drying characteristics.

13. The process of claim 4, in which the bodied ester is a bodied linseed oil.

14. The process of claim 4, in which the bodied ester is a bodied fatty oil, having a conjugated double bond in a fatty acid constituent.

15. The process of claim 4, in which the bodied ester is an alkyd resin, comprising in its acid component at least 50% of drying and semi-drying fatty acids.

16. The process of claim 4, in which step (*d*) of the process is carried out in a closed vessel, the

pressure in which is below that of atmospheric pressure.

17. The process of claim 4, in which, while step (*d*) is carried out, the emulsion is treated with X-rays.

18. The process of claim 4, in which, while step (*d*) is carried out, the emulsion is treated with ultra-violet rays.

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